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PATENT SPECIFICATION

Application Date: Feb. 25, 1935. *No. 6029/35.* **457,548**

Specification not Accepted

COMPLETE SPECIFICATION

Improvements in or relating to Lubricants

We, E. I. Du Pont De Nemours and Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to lubricants which are especially suitable for use in lubricating bearings and moving parts subjected to extremely high pressures, e.g. 20,000 pounds per square inch. Efficient lubrication depends upon the maintenance of a liquid film between the engaging parts and this requires a lubricant of high viscosity in order that the film may not be squeezed out of the narrow gap between the engaging parts. It is also necessary that this film of lubricant should be tenacious and that it should spread easily over the engaging surfaces.

Various additions have been made to lubricating oils with a view to obtaining the above mentioned desirable properties, e.g. sulphur, sulphur chloride, sulphurised oils or natural sulphur-containing oils, aluminium soaps, heavy metal soaps, castor oil, and aliphatic or aromatic halides. While some of these additions, such as sulphur and organic halides, greatly improve the lubricating properties of oils, they have not proved altogether satisfactory in use owing to their giving rise to corrosion. Such corrosion may be due to the addition themselves, or to their hydrolysis or oxidation products, and is often accentuated by the presence of small amounts of water.

We have found that organic esters of phosphorus acids possess excellent lubricating properties and are substantially free from objectionable corrosive action. Films containing these esters will adhere to metallic surfaces and resist very high pressures, so that they are particularly valuable for heavy duty bearings and high speed movements. Moreover, the films are tenacious and are not removed by contact with water, oil or organic solvents such as gasoline, naphtha and the like.

To give practical effect to this discovery, according to our invention, we provide a carrier for the phosphorus esters, which is preferably a liquid medium in which the ester is soluble or in which it can be dispersed or emulsified. Mineral, vegetable, animal or synthetic oils which themselves possess lubricating properties in a high degree, are especially suitable as liquid media, but we may also use liquids which are not generally regarded as lubricants, e.g. paraffin oil or neutral organic liquids of low viscosity, or even water.

Instead of a liquid medium we may use solid or semi-solid substances, e.g. graphite or greases. Moreover, we may employ porous bearing metals such as phosphor bronze which are impregnated with the phosphorus esters or with a medium containing the same. Such porous bearing metals may be used for journal bearings or for rubbing surfaces and do not require an additional supply of lubricant as that which exudes from the pores of the metal under the pressure to which it is subjected is sufficient to form an efficient film between the engaging surfaces.

Among the phosphorus esters which we have found to be particularly effective for our purpose are the aryl and aliphatic esters of phosphoric and phosphorus acids. Among the aliphatic esters, those containing a carbon chain of at least 8 carbon atoms have proved to be the most effective, and of these the mixed esters are generally preferred because of their greater solubility in lubricating oils and greases.

When the expression "long chain aliphatic (or alkyl)" is employed herein,

it will be understood that such expression means aliphatic or alkyl groups containing 8 or more carbon atoms. Also, when the term "phosphorus acids" is employed herein it will be understood that this term includes the various acids of phosphorus such as the various phosphoric, phosphorus and thio phosphorus acids. The term "bearing surfaces" as employed herein will be understood to mean surfaces which mutually carry a load and move relatively to each other.

The organic esters of the phosphorus acids may be employed as the free esters or as their alkaline salts such as the sodium, potassium, ammonium and organic amine salts. The addition of as small amount as 0.05% to an oil will have a noticeable effect. However, for practical use, it will generally be found desirable to use at least 0.2%. Further, the amount added to the oil or other carrier will be largely dependent upon the machinery in which it is applied and the area of the metal surfaces with which it will be brought into contact.

We have tested our improved lubricants by the method devised by J. O. Allmen (Oil and Gas Journal, 30, 109, 1931). This method consists in running a 1/4" diameter drill rod between two halves of a split bushing which is maintained stationary. The load on the bushing is controllable and provision is made for measuring the torque developed by the friction of the lubricant film. A hydraulic system for increasing the loading on the bushing until the oil film breaks and the metal seizes is provided. The rubbing speed is about 50 feet per minute and the method of loading is gradual, one weight being added to the loading lever each ten seconds. Each weight added to the loading lever increases the pressure on the bushing by about 125 lbs. The machine provides for beam loadings up to 20 weights which corresponds to a pressure of 20,000 lbs. per square inch on the full projected area of the drill rod. The bearing surface of the bushing is cut to a diameter 0.007 inch larger than the drill rod so that, before any wear occurs, the actual bearing surface is a line. As wear occurs, the bearing surface widens but seldom covers the bushing. After a test, the width of the bearing scar can be measured and an approximate value for the actual bearing pressure obtained. The values given in the following examples represent the calculated actual bearing pressures which were reached in the tests without failure f the film. These values represent film strength or film resistance.

When subjected to the above test, a good grade of paraffin oil will withstand a pressure of only 3 to 5000 lbs. per square inch. When an oil containing sulphur is tested by the sam method, such oil will show a film strength of about 20000 lbs. per square inch and will give a torque reading of over 4.0 lbs. ft. at this load.

EXAMPLE 1.

0.5% of dilauryl phosphate $(C_{12}H_{25})_2HPO_4$ was added to a medium viscosity mineral oil and the whole warmed slightly until the ester had dissolved. When tested by the method hereinbefore described, this oil showed a film resistance of more than 55,000 lbs. per square inch and the friction developed was 2.0 to 2.2 lb. ft. When larger amounts of the phosphate up to 4% were added to the same oil the same results were obtained.

EXAMPLE 2.

An oil mixture was made up as in Example 1, except that 1.0% of dicetyl phosphate was employed in place of the dilauryl phosphate. The load carried on test was more than 55,000 lbs. per square inch and the torque was 2.0 lb. ft.

EXAMPLE 3.

.5% of tricresyl phosphate was added to a medium viscosity mineral oil as in Example 1. The load carried on test was more than 25,000 lbs. per square inch and the torque developed was 3.5 lb. ft.

EXAMPLE 4.

1.0% of dicyclohexyl phosphate was added to a medium viscosity mineral oil. The load carried was 20,000 lbs. per square inch and the torque developed was 1.4 lb. ft.

EXAMPLE 5.

1% of dioleyl phosphate was added to a medium viscosity mineral oil. The load carried was 45,000 lbs. per square inch and the torque was 2.0 lb. ft.

EXAMPLE 6.

A lubricant made by dissolving 1% of dilauryl phosphate in a heavy oil withstood a pressure of more than 52,000 lbs. per square inch and developed a torque at this pressure of 2.2 lb. ft.

EXAMPLE 7.

A lubricant was prepared as described in Example 1, except that 1.0% of a mixture of di- and tri-lorol phosphites was employed in place of the dilauryl phosphate. The load carried on test was 51,000 lbs. per square inch and the torque at this load was 2.3 lb. ft.

The term lorol indicates a mixture of primary normal aliphatic alcohols of 8 and 10 carbon atoms which are obtained by fractionation of the alcohols resulting from the reduction of cocoanut and/or palm kernel oils. These alcohols had a

boiling range of 140 to 195° C. at 50 mm. Thus the term "lorol phosphites" means th phosphorous ester of such alcohols.

EXAMPLE 8.

One part of triphenyl phosphite ($(C_6H_5)_3PO_3$) mixed with 100 parts of a lubricating oil withstood a bearing pressure of 48,000 lbs. per square inch. The friction torque was 3.2 lb. ft.

EXAMPLE 9.

A medium viscosity mineral oil containing 1% of trinaphthyl phosphate carried a load of 21,000 lbs. per square inch, the torque was 2.2 lb. ft.

EXAMPLE 10.

A mixture was made up of one part dilorol phosphate and 99 parts of solvent naphtha. Under test, this lubricant withstood a pressure of more than 45,000 lbs. per square inch with a friction torque of 2.2 lb. ft.

EXAMPLE 11.

One part of dilorol phosphate was mixed with 99 parts of lorol alcohol, comprising a mixture of primary aliphatic alcohols containing 8 to 10 carbon atoms. This mixture withstood a load of 32,000 lbs. per square inch developing a torque of 2.1 lb. ft. Under the same conditions of test, a lorol alcohol film, in the absence of the phosphate, will break with less than 4,000 lbs. pressure per square inch.

EXAMPLE 12.

A mixed phosphate ester of lorol and ocenol tested alone withstood a bearing load of 45,000 lb. per square inch with a torque of 2.1 lb. ft.

Ocenol comprises a mixture of primary aliphatic alcohols containing 12 to 18 carbon atoms, having an iodine number of about 50 and is mostly oleyl alcohol.

EXAMPLE 13.

5.0% of a naturally occurring phosphate ester, lecithin, was added to a lubricating oil as in Example 1. On test, this mixture withstood a pressure of 52,000 lbs. per square inch and developed a torque of 3.0 lb. ft.

EXAMPLE 14.

One part of dilorol phosphate was mixed with 200 parts castor oil. This mixture withstood a pressure of 60,000 lbs. per square inch. The friction torque was 2.4 lb. ft.

EXAMPLE 15.

One part of dilorol phosphate was emulsified in 100 parts of water containing a small amount of caustic soda. This emulsion with stood a pressure of 32,000 lbs. per square inch with a friction torque of 1.9 lb. ft.

EXAMPLE 16.

One part of the α-naphthylamin salt of dilorol phosphate was mixed with 100 parts of lubricating oil. On test, this lubricant withstood a pressure of over 55,000 lbs. per square inch, at which load the friction torque was 2.4 lb ft.

EXAMPLE 17.

One part of dilauryl dithio phosphate was compounded with 100 parts of lubricating oil. The pressure carried was 34,000 lbs. per square inch. The torque was 2.1 lb. ft.

The above examples illustrate the results obtained with a few phosphorus esters. Other phosphorus esters which we have found to be effective for our purpose are: di-ethyl phosphate, triethyl phosphate, mixed cyclohexyl-cyclohexyl phosphates, tri-ocenol phosphate, di-octyl phosphate, mixed mono- and dilorol phosphates, mixed octyl lauryl phosphate (di-ester), tri-methylricinoleyl phosphate, lauroxy-ethanol phosphate, the monophosphate of the diglyceride obtained by partial hydrolysis of linseed oil, mixed phosphate esters of hydroxy stearic acid, cetyl-pyridinium phosphate, di-phenyl phosphate, di-cresyl phosphate, tri-nitrophenyl phosphate, tri-hexoxyphenyl phosphate, mixed tertiaryamylphenyl phosphates, mixed dodecahydrodiphenylol-propane phosphates, mixed mono- and di-decahydro-β-naphthyl phosphates, mixed tetrahydro-β-naphthyl phosphates, dilorol cresyl phosphate, dibutylamine salt of mixed phosphates of lorol, benzylamine salt of mixed phosphates of lorol, amylamine salt of mixed phosphates of lorol, mixed mono- and dibutyl phosphates, and in general the mono-, di- and tri-esters corresponding with any of those previously mentioned.

The above compounds are in general well known and the methods for making them are also well known and described in the literature. These methods generally comprise the treatment of alcohols, unsaturated aliphatic compounds or phenols with phosphorus chlorides or with phosphorous oxy chlorides or oxides. Accordingly, a detailed, description of the methods to be employed for making the compounds referred to is believed to be unnecessary. Mention may be made, however, of some other methods. Thus new esters of phosphorus acids may be obtained by the treatment of a mineral or natural oil with phosphorus halides and a catalyst such as aluminium chloride. Phosphate and phosphite esters can also be obtained by the treatment of oils containing ethylene linkages or hydroxyl groups with phosphorus halides, oxy halides, oxides or sulphides.

The fact that our improved lubricants retain their extreme pressure lubricating characteristics in liquids other than oils

and greases renders them particularly adapted for use as cutting oils, particularly in water emulsion. The use of cutting oils in machining operations is well known. The cutting fluid has two functions; the first to provide a lubricant to reduce the friction between the cutting tool and the work, and the second to provide a means for cooling the work.

The general practice is to use either an oil or a dispersion of oil in water. The oils used vary considerably depending on the particular operation and may vary from a light mineral oil to a heavy mixture of mineral and animal oils. The water suspensions are usually made up from oils by the addition of dispersing agents of the Turkey red oil type. Recently the practice of adding sulphur or sulphur compounds has become common.

Die shaping of sheet metals and drawing of sheets and wires and tubes has also recently been improved by the use of a lubricant between the contacting surfaces.

Cutting oils are now generally made up by compounding about 30 parts of lard oil, one to five parts of sulphur, two to ten parts of a petroleum sulphonate or Turkey red oil and about 60 parts of mineral oil. This mixture is then used undiluted or dispersed in water which improves its cooling properties.

The lard oil, of course, breaks down under the high temperature conditions of use resulting in the formation of disagreeably odorous materials. The presence of sulphur, as in motor and gear lubricants, is a possible source of corrosive material necessitating the careful washing of machined parts before use. These oils have also given considerable trouble from infection of the workmen which is only partially eliminated by the incorporation of a bactericide in the oil.

Wire drawing also requires an extreme pressure lubricant. Several types are in use but essentially they are the same as the ordinary cutting oils.

The pressures between the rubbing surfaces during all machining operations are obviously very high as they result in deformation of the metal. This is, therefore, another problem of extreme pressure lubrication.

Our lubricants may be used in water, oil or other suitable media as cutting oil compositions with the attending elimination of the odours and corrosiveness which are objectionable properties of most prior cutting oils. They will be effective at very low concentrations in oil and can be used in water directly without the use of an oil medium.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An improved lubricant, especially suitable for lubricating heavy duty bearings and high speed movements, comprising an organic ester of a phosphorus acid associated with a suitable carrier of the kind hereinbefore described.

2. A lubricant as claimed in claim 1, in which the carrier is a liquid medium in which the phosphorus ester is dissolved, dispersed or emulsified.

3. A lubricant as claimed in claim 1, in which the carrier is a lubricating oil.

4. A lubricant as claimed in claim 1, in which the carrier is a solid or semi-solid material such as graphite or grease.

5. A lubricant as claimed in claim 1, in which the carrier is a porous bearing metal.

6. A lubricant as claimed in any of claims 1—5, in which the ester is an aryl ester.

7. A lubricant as claimed in any of claims 1—5, in which the ester is a long chain aliphatic ester.

8. A lubricant as claimed in claim 7, in which the ester is a long-chain alkyl ester.

9. A lubricant as claimed in claim 7 or 8, in which the ester is a mixed ester.

10. A lubricant as claimed in any of claims 1—9, in which a mixture of esters of phosphorus acids is associated with the carrier.

11. A lubricant as claimed in any of claims 1—10, in which the proportion of ester relative to carrier is small, e.g. 0.2—5 per cent.

12. Improved lubricants, substantially as hereinbefore described, with reference to the examples.

Dated the 25th day of February, 1935.

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